(12) UK Patent Application (19) GB (11) 2 165 342 A

(43) Application published 9 Apr 1986

(21) Application No 8524187

(22) Date of filing 1 Oct 1985

(30) Priority data
(31) 59/204036 (32) 1 Oct 1984 (33) JP

(71) Applicants
Nichias Corporation (Japan),
1–26 Shiba Daimon 1-chome, Minato-ku, Tokyo, Japan.
Honshuseishi Kabushiki Kaisha (Japan),
12–8 Ginza 5-chome, Chuo-ku, Tokyo, Japan

(72) Inventors
Michio Nishiyama
Shigeo Take
Isao Terada
Kazuyuki Naoi
Masaji Kurosawa
Hitoshi Tanaka
Setsuo Toyoshima

(74) Agent and/or Address for Service
Phillips & Leigh,
7 Staple Inn, Holborn, London WC1V 7QF

(51) INT CL[4]
F28C 3/02

(52) Domestic classification
F4K 25U

(56) Documents cited
None

(58) Field of search
F4K

(54) Heat-exchanging element for gaseous media

(57) A heat-exchange element is provided of the type in which a honeycomb-like structure is formed of inorganic fiber. The fiber used in the invention is glass fiber containing 5–25% by weight zirconium oxide. This gives improved resistance to acid and alkali attack by condensed gases or other components of the heat-exchange element.

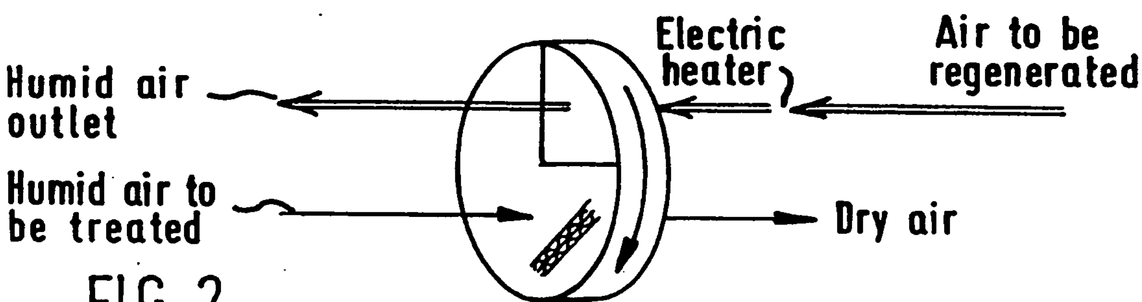

FIG.2

GB 2 165 342 A

BEST AVAILABLE COPY

2165342

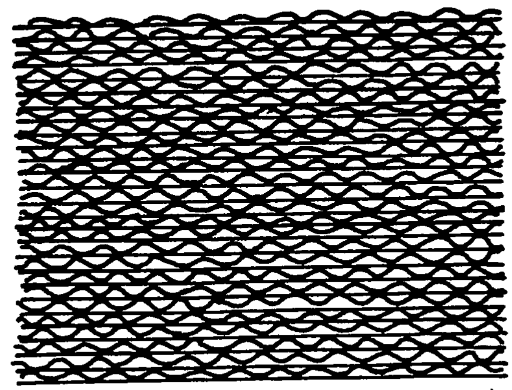

FIG.1

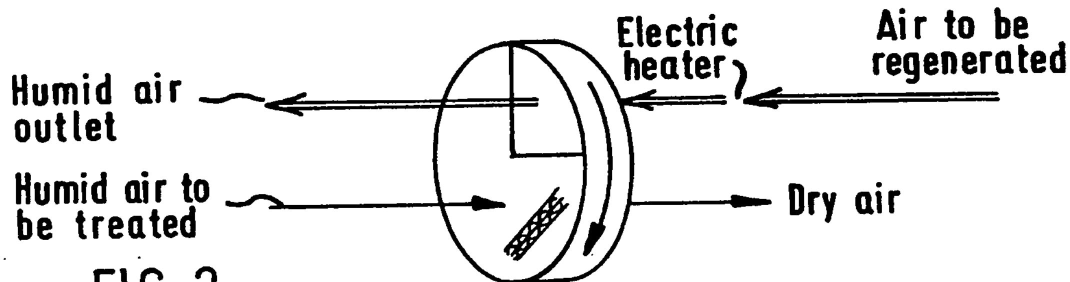

FIG.2

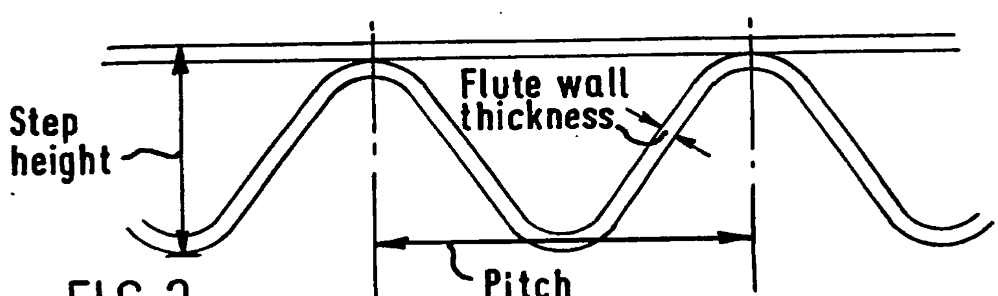

FIG.3

SPECIFICATION

Heat-exchanging element for gaseous media

This invention relates to improved heat-exchange elements for gaseous media, and particularly to heat-exchange elements for exchanging latent heat and/or sensible heat between gases.

Heat-exchanging elements for gaseous media having a honeycomb-like structure, made of a paper which is chiefly composed of organic fibers or inorganic fibers, have been widely known as disclosed in Japanese Patent Publication Nos. 127663/1977 and 19548/1979. Compared with the heat-exchanging elements of honeycomb-like structure obtained by extrusion-molding ceramic materials, the heat-exchanging elements of this type are light in weight and can be constructed in large sizes, and are advantageous from the standpoint of produceability, and have therefore been placed in practice in various fields of applications.

From the standpoint of applications, heat-exchanging elements for gaseous media can be roughly divided into elements for exchanging sensible heat, elements for exchanging latent heat (for removing or reducing moisture), and elements for exchanging total heat (sensible heat as well as latent heat). The elements for exchanging the latent heat and total heat carry a hygroscopic agent such as lithium chloride, lithium bromide, molecular sieve, or the like. In the case of heat-exchanging elements made of paper, the fibers that are heretofore used as chief materials for producing paper include:– organic fibers such as cellulose fiber, synthetic fiber; asbestos; ceramic fibers such as fiber containing silica, fiber containing silica and alumina, fiber containing silica, alumina and chromium, and fiber containing silica, alumina and zirconia; and glass fiber (electrical glass fiber). These fibers are used depending upon the purposes and conditions in which the heat-exchanging element is used, and depending upon the difficulty of making paper and of making the honeycomb-like structure.

Such heat-exchanging elements having a honeycomb-like structure obtained by using a paper develop problems in regard to resistance against heat, and durability when they are used under severe conditions for exchanging sensible heat and latent heat, if heat-exchanging performance is put aside.

In the case of the heat-exchanging element for exchanging sensible heat, for example, if gases containing sulfur oxides are treated in the temperature range 80–200°C, the sulfur oxides can condense and adhere onto the heat-exchanging element. Therefore, the heat-exchanging element must have resistance against acids in addition to resistance against the heat. However, the conventional heat-exchanging elements that employ asbestos, electrical glass fiber, and ceramic fiber containing silica and alumina, are not quite satisfactory in this regard, and are not utilizable for treating gases that contain sulfur oxides. In the case of heat-exchanging elements for exchanging latent heat the paper must carry a hygroscopic agent. However, lithium chloride or lithium bromide that is most commonly used as a hygroscopic agent corrodes the fiber that constitutes the paper at a regenerated gas temperature of around 100° to 150°C to deteriorate the properties of the paper. Therefore, problems arise in regard to resistance against the action of lithium chloride or lithium bromide (hereinafter referred to as resistance against lithium chloride) under the above-mentioned conditions. Papers made of asbestos exhibit good resistance against lithium chloride. However, papers made of electrical glass fiber or ceramic fiber exhibits poor resistance and fails to produce its proper function within short periods of time.

The object of the present invention is to provide a heat-resistant heat-exchanging element that can be easily produced without using asbestos, and that exhibits excellent resistance against acids and lithium chloride, in view of the fact that the conventional heat-exchanging elements are not satisfactory with regard to resistance against acids and lithium chloride as mentioned above imposing limitations on their applications in spite of their numerous advantages compared with the heat-exchanging elements of other systems, and that it has been desired not to use asbestos because of environmental and sanitary reasons.

The inventors have found that the durability of the heat-exchanging element is mostly dependent upon the kind of fibers that are chief materials of the paper, though it is also affected by the kind of paper and microstructure thereof to some extent. The inventors have further found that a glass fiber containing zirconium oxide is generally superior to other inorganic fibers in regard to resistance against acids and against lithium chloride. Glass fiber containing zirconium oxide has been known to exhibit excellent resistance against alkali. To utilize such a merit, therefore, glass fiber containing zirconium oxide has heretofore been chiefly used for reinforcing cement products. However, the fact that this fiber exhibits resistance against acids as well as against lithium chloride has not been known, and this fiber has not ever been used for the production of heat-exchanging elements.

The present invention provides a heat-exchange element for gaseous media comprising a honeycomb-like structure made of a paper comprising an inorganic fiber, characterised in that the inorganic fiber comprises a glass containing 5 to 25% by weight of zirconium oxide.

The fiber containing zirconium oxide employed by the present invention will be described

below in furter detail with reference to the drawings in which:

Figure 1 illustrates a typical example of honeycomb-like structure referred to above;

Figure 2 illustrates a rotary heat-exchanger element as described in the examples below; and

Figure 3 schematically illustrates terms used in the text.

As mentioned above, this fiber has been widely known to exhibit resistance against alkali, and has been placed in the market and is easily available. Concrete examples of the commercially available fibers that can be used include ARfiber (Asahi Glass Co.), CEM-FIL (Pilkington Co.) and many other products produced by Nippon Denki Glass Co., Nittobo Co., Central Glass Co. A preferred range of glass composition containing zirconium oxide is as follows (numerals in parenthesis represent particularly preferred ranges):

SiO_2	50 to 70% by weight
ZrO_2	5 to 25% by weight
	(15 to 25% by weight)
Al_2O_3	0 to 10% by weight
oxides of alkaline earth metals, MnO_2	0 to 20% by weight
oxides of alkali metals	10 to 25% by weight
remainder	0 to 5% by weight

There is no particular limitation imposed on the heat-exchanging element of the present invention except that use is made of a fiber containing zirconium oxide as mentioned above. That is, no particular limitation is imposed on other materials used or present on the coating material used for processing the paper, on the hygroscopic agent or on the adhesive agent. Further, no limitation is imposed on the honeycomb-like structure. It needs not be pointed out, however, that materials other than the fiber should be selectively used in order to improve the resistance against acids and lithium chloride of the heat-exchanging element as much as possible.

Described below is a representative method of producing a heat-exchanging element according to the present invention.

First, a fiber containing zirconium oxide is prepared in the form of a paper according to a conventional method of making glass-fiber paper. Preferably, the paper should have a thickness of about 0.15 to 1.0 mm and a basis weight of about 15 to 200 g/m². The paper that is fresh prepared has too large a gas permeability and should hence be applied with a coating (filler) to impart gas blocking property that is required when the paper serves as a partitioning wall of the heat-exchanging element. The coating is further effective to improve the processability of the paper and to increase the density of the product so that it has an increased heat capacity. As the coating material for this purpose, use is made of a mixture consisting of an organic binder such as vinyl acetate resin, ethylene-vinyl acetate copolymer, polyethylene, water-soluble acrylic resin, water-soluble polyurethane resin, vinyl chloride resin, vinylidene chloride resin, polyvinyl alcohol resin, starch, oxidized starch or casein, and an inorganic filler having a particle size of smaller than 20 μ and preferably having a particle size of from about 0.5 to about 10 μ. Examples of the filler that can be used include clay minerals (such as mica, talc, kaolin and the like), crystalline silica powder such as silicic anhydride, amorphous silica powder such as white carbon, as well as titanium oxide, zircon sand powder, barite powder, zirconia powder and the like. Clay minerals are suited for exchanging the latent heat and the total heat, and others are suited for exchanging the sensible heat. The amount of coating material applied usually ranges from about 50 to about 500 g/m² reckoned as a solid content, and should be suitably adjusted depending upon the thickness of the paper and the applications in which the product is used.

The paper after the coating has been finished is dried, and is subjected to the forming such as corrugate processing that is necessary to produce a honeycomb-like structure. To obtain a heat-exchanging element of a desired shape, furthermore, the processed paper and unprocessed paper are laminated upon one another. For instance, a wind-up processing is effected to obtain a heat-exchanging element of the rotary heat-exchanger. Fig. 1 shows an example after these processings have been finished. The laminate should not be obtained by using an organic adhesive agent, but should be obtained by using an inorganic adhesive agent that can withstand

the baking that will be described later. Preferred examples of the adhesive agent include:

(1) Alumina sol to which are added bentonite, kaolin, silica powder and the like to adjust the viscosity, water-retaining property, and initial adhesiveness;

(2) Colloidal silica to which are a ded bentonite, kaolin, silica powder and the like to adjust the viscosity, water-retaining property and initial adhesiveness, and

(3) Sodium silicate to which are added bentonite, kaolin, silica powder and the like to adjust the viscosity, water-retaining property and intitial adhesiveness (all of which being diluted with water).

The paper which has been molded and laminated is then uniformly impregnated with a hardening agent such as colloidal silica or sodium silicate. The paper is then dehydrated, subjected to the blow of air, dried by the air, and is baked by air to remove organic components contained in the paper and in the adhesive agent. Preferably, the paper is impregnated again with the hardening agent and is dried to obtain the heat-exchanging element of the present invention.

The thus obtained heat-exchanging element is used in its own form, or is subjected to the cutting, perforation or again to the adhesion to obtain the heat-exchanging element having required size, shape and construction. The heat-exchanging element that is to be used for exchanging the latent heat or the total heat, is immersed in a lithium chloride solution or lithium bromide solution at any stage after the step of baking so that it carries a hygroscopic agent composed thereof.

The heat-exchanging element of the present invention exhibits excellent resistance against acids and against lithium salt, since a glass fiber containing zirconium oxide which is a chief material of the paper exhibits a high degree of resistance against acids and lithium chloride. The heat-exchanging element further exhibits good resistance against the heat. Therefore, the heat-exchanging element of the invention is deteriorated little even when it is used for exchanging the sensible heat or latent heat of gasses containing sulfur oxides, and can hence be used for extended periods of time.

Example 1:

A paper having a thickness of 0.16 mm and a basis weight of 22 g/m² was prepared from a zirconium oxide-containing glass fiber (average fiber length of 9 mm) ahving a glass composition of 17% by weight of ZrO_2, 62% by weight of SiO_2, 5% by weight of Na_2O+K_2O, and 16% by weight of CaO, and was coated with a clay (kaolin) in an amount of 80 g/m² (using a coating agent with polyvinyl alcohol as a binder). Then, the paper coated with clay thus obtained was overlapped on the same paper but which has been corrugated by a corrugating machine that produces corrugated carboard, and the laminated papers were wound up in the form of a rotor while imparting an adhesive agent. After the adhesive agent is dried, the rotor-like molded product was removed from the winding machine, and was immersed in a colloidal silica solution having a solid content of 30% by weight for 30 minutes. Thereafter, the silica was dried and cured at 100°C, and was then heated at 400°C for one hour while circulating the air to decompose organic components. The fired product was immersed again in the colloidal silica solution, and was dried at 200°C to obtain a rotor-like heat-exchanging element having a diameter of 1500 mm. The heat-exchanging element possessed a flute wall thickness of 0.21 mm, a step height of 1.97 mm, a pitch of 3.3 mm and a density of 230 kg/m³. The terms "step height", "flute wall thickness" and "pitch" are made clear by Fig. 3.

The above heat-exchanging element was immersed in a lithium chloride solution to obtain a latent heat-exchanging element that carried 14% by weight of lithium chloride as a hygroscopic agent. The heat-exchanging element was used for one year being installed in a latent heat-exchanger for supplying dry air in the steel industry. The heat-exchanging element exhibited sufficiently high latent heat-exchanging function, and the physical properties were not deteriorated to a serious degree.

Example 2:

Using the same glass fiber as that of Example 1, the steps were carried out up to forming a rotor-like heat-exchanging element in the same manner as in Example 1. The obtained rotor-like molded product was immersed in a curing solution consisting of 70 parts by weight of sodium silicate No. 3 (Sodium Silicate No. 3 being a generally used technical term for a silicate having a SiO_2/Na_2O mole ratio of 3) and 30 parts by weight of water for 30 minutes and then, after being dried at 170°C the organic components were decomposed by being heated at 400°C for 1 hour while circulating the air. The fired product was immersed again in said curing solution and was dried at 400°C to obtain a rotor-like heat-exchanging element having a diameter of 1500 mm. The heat-exchanging element possessed a flute wall thickness of 0.20 mm, a step height of 1.95 mm, a pitch of 3.3 mm and a density of 220 kg/m³.

The above heat-exchanging element was immersed in a lithium chloride solution to obtain a latent heat-exchanging element that carried 14% by weight of lithium chloride as a hygroscopic

agent. The heat-exchanging element was used for one year being installed in a latent heat exchanger for supplying dry air in the plastic film industry. The heat-exchanging element exhibited sufficiently high latent heat-exchanging function, and its physical properties were not deteriorated to a serious degree.

Example 3:

A paper having a thickness of 0.5 mm and a basis weight of 50 g/cm² was prepared from a zirconium oxide-containing glass fiber (average fiber length of 13 mm) having a glass composition of 20% by weight of ZrO_2, 58% by weight of SiO_2, 1% by weight of Al_2O_3, 4% by weight of B_2O_3, and 17% by weight of CaO, and was coated with a powder of silicic anhydride in an amount of 300 g/m² (using a coating agent with water-soluble acrylic resin as a binder). Then, the coated paper thus obtained was overlapped on the same paper but which has been corrugated by a corrugating machine that produces corrugated cardboard, and the laminated papers were adhered together. The thus obtained laminate which was corrugated on one surface only was laminated upon one another with the flute direction thereof at right angles with one another. After the adhesive agent was dried, the laminate was cured in the same manner as in Example 2 to obtain a sensible heat-exchanging element of the heat transmission type of a square shape each side measuring 600 mm. The element possessed a wall thickness of 0.7 mm, a step height of 7 mm, a pitch of 12 mm, and a density of 350 kg/m³.

The heat-exchanging element was used for one year being installed in a sensible heat exchanger to recover the heat from the waste gas of a boiler. The heat-exchanging element exhibited a heat-exchanging efficiency of 60% in average, and its properties were not almost deteriorated.

Comparative Test (1):

Papers (0.18 to 0.20 mm thick) composed of electrical glass fiber, C-glass fiber, ceramic fiber containing silica and alumina or zirconium oxide-containing glass fiber (having a glass composition of 17% by weight of ZrO_2, 62% by weight of SiO_2, 5% by weight of Na_2O+K_2O, 16% by weight of CaO) were coated with clay in the same manner as in Example 1, and were corrugated maintaining a pitch of 3.3 mm. Each of the corrugated papers was then superposed on the flat coated paper which has not been corrugated and was adhered thereto to obtain a corrugated laminate which was corrugated on one surface only. The laminate was then overlapped on one another with the flute directions thereof being in alignment. The thus obtained laminate was then cured in the same manner as in Example 1 to obtain a heat-exchanging element for testing. However, the paper composed of the ceramic fiber was not coated with clay.

The heat-exchanging elements were then tested for their resistance against acids and against lithium chloride under the conditions mentioned below. Table 1 shows the results together with the densities of elements.

In the resistance test against acids the elements were immersed in sulfuric acid of a concentration of 10% heated at 95°C for 48 hours, and compressive strengths in the flute direction were compared before and after the immersion.

In the resistance test against lithium chloride the elements were immersed in an aqueous solution of lithium chloride of a concentration of 40% heated at 125°C for 48 hours, and compressive strengths in the flute direction were compared before and after the immersion.

Table 2

	Element density (kg/m^3)	Buckling strength (kg/cm^2)				Remarks
		Before test	After three months	After six months	After twelve months	
E-glass fiber	225	14.1	12.3	5.6	-	Deteriorated and clogged after 6 months
C-glass fiber	228	14.4	10.0	5.4	-	" " after 5 months
Ceramic fiber	195	15.1	4.7	-	-	" " after 3 months
ZrO_2-containing glass fiber	230	14.7	13.5	13.0	12.8	Not deteriorated or clogged

Comparative Test (2):

Heat-exchanging elements obtained in the same manner as in Comparative Test (1) were tested for their resistance against lithium chloride under the conditions described below.

These elements were formed in the shape of a rotor which was corrugated maintaining a height of 1.97mm, a pitch of 3.3 mm, and having an outer diameter of 360 mm and a thickness of 200 mm.

The elements were impregnated with a solution containing 14% by weight of lithium chloride, and were then tested as described below.

Humid air to be treated (heated at 33°C, 70% RH) was passed through three-fourths of the element, so that the element absorbed the moisture to obtain the dry air. The element was kept turing at a speed of 14 turns an hour, so that the moisture in the element was taken out with the air to be regenerated (heated at 130°C, 3% RH) that was passed through one-fourth of the element. Both the treated air and the regenerated air were blown at such a rate that the air speed through the corrugate was three meters a second.

The element was removed from the heat exchanger after every month. Results of observations were as shown in Table 2, in which the buckling strength shows the strength at that point in time when a 10 cm square cube cut out of the element first buckles after a load is directly applied in the direction of lamination.

Table 1

Fiber	Element density (kg/m³)	Initial stregnth (kg/m²)	Resistance against acid		Resistance against lithium chloride	
			Strength after immersion (kg/cm²)	Reduction of strength (%)	Strength after immersion (kg/cm²)	Reduction of stregnth (%)
E-glass fiber	225	14.1	5.5	61	6.5	54
C-glass fiber	228	14.4	13.7	5	5.5	62
Ceramic fiber	195	15.1	6.2	59	6.9	54
ZrO_2-containing glass fiber	230	14.7	13.7	[illegible]	13.5	8

CLAIMS

1. A heat-exchange element for gaseous media comprising a honeycomb-like structure made of a paper comprising an inorganic fiber, characterised in that the inorganic fibre comprises a glass containing 5 to 25% by weight of zirconium oxide.

2. A heat-exchange element as set forth in Claim 1, wherein the glass constituting the inorganid fiber has a composition comprising 5 to 25% by weight of zirconium oxide, 50 to 70% by weight of silica, 10 to 30% by weight of oxides (total amount) of alkali metals, alkaline earth metals or manganese, and less than 10% by weight of other components.

3. A heat-exchange element as set forth in Claim 1, wherein the paper carries lithium chloride or lithium bromide as a hygroscopic agent.

4. A heat-exchange element as claimed in Claim 2 in which the glass has a composition (% by weight):

SiO_2	50 - 70%
ZrO_2	5 - 25%
Al_2O_3	0 - 10%
oxides of alkaline earth metals, MnO_2	0 - 20%
oxides of alkali metals	10 - 25%
remainder	0 - 5%

5. A heat-exchange element as claimed in Claim 4 in which the glass contains 15–25% by weight zirconium oxide.

6. A heat-exchange element as claimed in Claim 1 and substantially as described.

Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1986, 4235.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.